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(54) Title: MATERIALS FOR POLYMER OPTICAL FIBERS

(57) Abstract: The use of an at least partially polymerised preform having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes for drawing into a fibre having a corresponding cross-section, and wherein said first discrete region is formed from an optically suitable material which includes at least one functional species dispersed therethrough, and the second discrete region may be a void. The preform is a precursor to a holey polymer fibre, which has a refractive index gradient cross-section. The holey polymer fibre may have dispersed species with functional capability, such as rare earth optical amplifiers. Unlike prior art methods, the method of the present application allow the functionalisation and refractive index grading steps to be carried out independently.

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TITLE: "MATERIALS FOR POLYMER OPTICAL FIBERS"

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TECHNICAL FIELD

The invention relates to polymeric materials for use in optical fibers and optical devices. In particular, the polymeric materials of the present invention are for use in optical fibers and optical devices made from preforms.

20 BACKGROUND ART

Polymer optical fibers (POF's) work by guiding light through optically transparent polymers. The light is guided by the formation of a refractive index profile in the polymer fibre. It has previously only been known to create such refractive index profiles by the use of at least two materials in the polymer fibre with differing refractive index - a low
25 refractive index cladding, and a higher refractive index at the core of the fibre. The two materials can be two different polymers, or a single polymeric material can be used with a small molecule 'dopant' used to change the refractive index profile.

The exact methods of manufacture of polymer optical fibers depends upon the intended use of the fibers. When a POF is used as an illumination fibre, i.e. for the
30 transmittance and emittance of light for display and lighting purposes, it is generally made by a one or two-step process. In the single step process, two polymer materials are co-extruded through a polymer extruder die, thus forming the fibre. The two-step process involves the manufacture of a pre-form with the required refractive index profile (two

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materials), but in a much larger size than the fibre. This pre-form is then heated and a smaller diameter fibre is drawn from it.

When POF's are used for the transmission of data, generally the two-step manufacturing process is used. However, for data transmission purposes it is critical that the absorption and scattering of light within the fibre be minimized; in fact, the ideal situation is that there is no absorption or scattering of light. In order to achieve this the polymer materials that are used are generally highly purified.

For data transmission purposes the desired properties of a POF is that there can be made a large core fibre that is mechanically flexible. The large core fibre allows easy and inexpensive connectivity of fibers during installation, in contrast to small core glass optical fibers, which require costly sub-micron connectivity precision. Polymers allow large core fibers to be mechanically flexible, since polymers have lower Young's moduli than silica glass; this property allows large core polymer fibers to bent around tight corners in home and office installations, and also allows more rigorous handling during installation.

Traditionally, large core polymer fibers are multi-moded, and in order to reduce modal dispersion within the fibre it has been necessary to manufacture graded index multi-mode POF. Additionally, in order to reduce loss in graded index fibre it has been necessary to use polymers and dopant(s) to create the refractive profile, rather than two polymers.

A more exacting refractive index profile can be achieved in this way, where two polymers or a polymer and a dopant are polymerized together, and via kinetic and thermodynamic means there is produced a refractive index profile, where the materials have a concentration profile, and are co-located in the fibre.

However, polymers are generally not thermodynamically miscible, and in order to get a graded index profile utilizing two miscible polymers one is restricted to a very limited set of truly miscible polymers. Unfortunately it is also very important to use low

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loss polymers, and the limited number of pairs of truly miscible polymers is of polymers that are generally not the lowest loss polymers available. Additionally, two polymer systems also increase the possibility of scattering of light from micro-domains of polymers. Hence, most graded index POF systems generally use a polymer and a dopant.

5 This allows the use of a purpose developed low loss polymer.

However, the use of a dopant also creates some restrictions on POF manufacture and cost. First, in order to get a graded index profile, the polymers are restricted to free radical polymers. Second, in order to ensure that the dopant does not diffuse at operating temperature it has been necessary to use polymers with very high glass transition
10 temperatures. Third, the development of low loss, high glass transition temperature polymers has meant the use of very expensive polymers. Finally, the process of making the graded index fibers relies on a combination of kinetics and thermodynamics, and is a process that does not lend itself to easy commercialisation, and is also very expensive.

All these factors mean that in order to form functioning POF's, the requirements of
15 the preparative process precluded the use of many polymeric substances which would otherwise impart a variety of very desirable properties on any subsequent POF.

As described in our co pending application PCT/AU02/00638, "holey POF's" may be shaped from "holey preforms" of a predetermined configuration. The configuration of the holes in the preform can be used to give fibers which incorporate precisely engineered air
20 gaps. Holey fibers differ significantly from traditional glass fibers and POF's in that the light is not guided by a refractive index profile created by the use of two solid materials, but rather light is guided by the use of a polymeric material (which may be a single polymeric component) and air holes.

It is the location and nature of these holes that dictate the refractive index profile and
25 light guiding nature of the POF

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In one case, light may be guided in Holey fibers by the overall refractive index profile of the fibre. In this case, the center of the fibre is a core of solid material with holes running along the length of the fibre create an overall refractive index profile that guides light as it does in fibers containing two materials.

5 Alternatively, light may be guided by a photonic bandgap formed from the orientation of the holes. In the case of band-gap fibers, the core guiding section of the fibre is an air hole. It will be appreciated that in the second case very low loss of light is expected. However, bandgap structures in fibers are very difficult to make, as they require very high accuracy and precision of holes in the fibers, which must be continued along the
10 length of the fibers. To date, it has been very difficult to make glass bandgap fibers that transmit light more than a few meters without suffering large losses due to scattering and other loss mechanisms. This has been because the fibers have been made from glass, where a pre-form is made by fusing glass capillaries, and then drawing down the thus-formed pre-form at very high temperatures (ca. 1800°C). At these high temperatures processing is
15 expensive and inflexible and the air and/or gas volatility make even and reproducible hole structures difficult to manufacture.

In PCT/AU02/00638, the disclosure of which is incorporated herein by reference, the present applicant has described new holey fibers and processes for their preparation. This process entails providing a preform of polymeric material of predetermined holey
20 cross-section and drawing this into a holey fibre.

It is now possible to control the refractive index properties of a POF by changing the mechanical shape of the preform. This means that it is no longer necessary to seek to control the refractive index property by variation of the chemistry of the starting materials. In effect, the holey fibre method opens the possibility of the use of just about any
25 polymeric material in a POF.

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It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common
5 general knowledge in the field.

DESCRIPTION OF THE INVENTION

It has been found by the present applicants that the method of drawing holey fibers from holey preforms enables control of the refractive index profile in the fibre, thus allowing the hitherto un contemplated use of polymers which have been fully or at least
10 partially polymerised as preforms.

According to a very broad aspect, the invention provides the use of an at least partially polymerised preform having a predetermined cross-section with at least two discrete regions with non identical refractive indexes for drawing into a fibre having a corresponding cross-section. At least one of the regions is formed from an optically
15 suitable material.

By predetermined cross section is meant any cross section which is formed in order to act in part or in full as a means to control the light transmission properties of a fibre. In preferred embodiments, at least one of the other discrete optical elements is a void.

20 The invention also relates to a holey polymer optical fibre prepared from either a fully or partially polymerised preform.

According to a first aspect, the invention provides the use of an at least partially polymerised preform having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes for drawing into a
25 fibre having a corresponding cross-section, and wherein said first discrete region is formed

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from an optically suitable material which includes at least one functional species dispersed therethrough.

Preferably, the second discrete optical element is a void.

According to a second aspect the invention provides a drawable polymer preform
5 having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material which includes at least one functional species dispersed therethrough.

Preferably, the second discrete region is a void and the predetermined cross-section
10 is a precursor profile for a holey polymer fibre.

Preferably, the polymer is selected from the group consisting of polymethyl methacrylate, polymethylmethacrylate/polystyrene, siloxane, fluoropolymers, fluoroacrylates, fluoroacrylate esters, fluorinated polyimides, polytetrafluoroethylene, fluorosilicones CYTOPTM and THVTM.

15 According to a third aspect, the invention provides a drawable polymer preform having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material which includes at least one functional species bound thereto.

20 According to a fourth aspect the invention provides a drawable polymer preform having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material which includes at least one reactable functionality.

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The reactable functionality may be on a polymeric component or on a monomeric component.

Preferably, the functional species is dispersed evenly throughout the preform and/or fibre. In a preferred alternative, the functional species is dispersed throughout the preform
5 and/or fibre in a predetermined pattern.

Preferably, the functional species is an atomic species. More preferably, the functional species is a light amplifying species. Most preferably, the functional species is one or more of erbium, praseodymium or tantalum. These species can be usefully used in the amplification of optical light, and when placed in fibre can form optical fibre
10 amplifiers.

According to a fifth aspect the invention provides a polymeric optical fibre having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material which includes at least one functional species
15 dispersed therethrough.

Preferably the second discrete optical element is a void. Preferably, the polymeric optical fibre has a graded refractive index profile and is a multimode fibre.

Preferably, the polymer is selected from the consisting of polymethyl methacrylate, polymethylmethacrylate/polystyrene, siloxane, fluoropolymers, fluoroacrylates,
20 fluoroacrylate esters, fluorinated polyimides, polytetrafluoroethylene, fluorosilicones CYTOP™ and THV™.

Preferably, the functional species is an optical property modifier, more preferably selected from fluorescing species, electro-optic, acousto-optic, magneto-optic or piezo-optic species.

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In alternative preferred embodiments, the dispersed species is a mechanical property modifier, such as a plasticiser or surfactant.

The polymeric optical fibre may also be formed from a polymer having groups capable of interacting with said functional species, such as pendant chelating groups and/or
5 acid groups.

In one highly preferred embodiment, the functional species is an optical amplifier, most preferably one or more rare earth element, for example, one or more of erbium, praseodymium or tantalium, in preferably complexed form, with one or more organic ligands, or uncomplexed form.

10 If the rare earth is complexed, the preferred ligands are selected from phenanthroline, bipyridine, or beta diketone ligands, and most preferably the ligand is 6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (FOD). In some preferred forms, the functional species is EuFOD or ErFOD.

The elements encompassed by the term "rare earth" are well known to chemists and
15 include those elements classified as either lanthanides or actinides, as well as scandium and Yttrium.

The lanthanides include Lanthanum, Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium,
Erbium, Thulium, Ytterbium, Lutetium.

20 The actinides include Actinium, Thorium, Protactinium, Uranium, Neptunium, Plutonium, Americium, Curium, Berkelium, Californium, Einsteinium, Fermium, Mendelevium, Nobelium, Lawrencium.

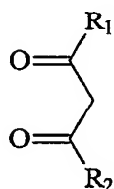
The rare earth metal may be in particulate form, or, more preferably, in complexed form, especially with organic ligands. Virtually any form of organic ligand which will
25 allow dispersion of the rare earth metal through the polymer will be suitable. Especially

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suitable are ligands such as phenanthroline or bipyridine, or those ligands based around beta diketones.



Examples of beta diketones are shown below.

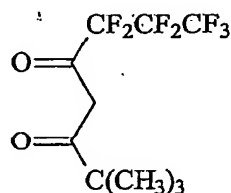


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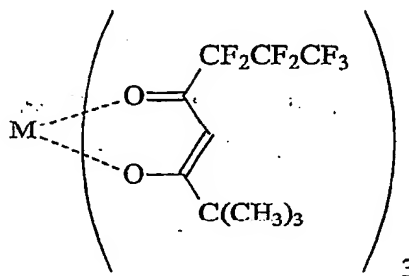
Where R1 and R2 may independently be an alkyl group, for example selected from methyl, ethyl, propyl, butyl, isopropyl or tert butyl, or a fluorinated analogue, such as a trifluoromethyl, a pentafluoroethyl or a hepta fluoropropyl, or an aromatic group such as phenyl, naphthyl, anthracenyl, phenanthryl, or a hetero analogue thereof substituted with one or more elements such as N, S, O or P

10

One particularly preferred form of beta diketone is 6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, or FOD.



Uncomplexed Ligand



MFOD

15 Rare earth FODs, in particular EuFOD and ErFOD are commercially available as chemical shift reagents to aid in the analysis of complex NMR spectra.

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The present invention is not limited to those specific active species given here by way of example. In the case of rare earth amplifying agents, the ligand is chosen for its ability to disperse the metal throughout the polymer, ie to render it chemically compatible with the polymeric material. The ligand also serves to ensure that metal to metal electronic interactions are minimised, ie the ligands in effect act as the determinant of the minimum possible spacing between metal centres. In the case of the rare earth compounds of the present invention, the ligands also affect the electronic structure of the central metal, which in some circumstances is necessary to enable it to function as desired.

As the optical data signal moves down a fibre, the signal becomes attenuated with distance. A rare earth species dispersed throughout the optical fibre can be put into an excited state by the introduction of pump light (by, for example, a semiconductor laser). The excited rare earth species then synchronises with the incident optical data signal and emits photons at the input signal energy. By this process, amplifications of the signal of ten or a hundredfold or more are possible.

Other suitable species which may be used to "cage" and disperse species such as rare earth metals include divergently synthesised compounds, such as dendrimers. The use of silane/siloxane dendrimers is particularly contemplated.

Other systems which exhibit self assembly around metal centres are also suitable for complexing metallic species, such as amine/ether assemblies.

Rare Earth metals (including Lanthanides) are known to be optical amplifiers, absorbing energy at one wavelength and emitting it at another, more desirable wavelength. The use of rare earth metals in POFs (polymer optical fibres) is known to be a desirable goal to those skilled in the art, and has been contemplated previously in US 5,657,156 and 5,027,079 for example. All the rare earth amplifying species disclosed therein are suitable for use in the present application. While the prior art contemplates the use of certain rare

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earth metals as amplifiers, they do not disclose or suggest the use of an active species disclosed in a POF which has a stepped or graded refractive index profile (which is critical for the production of multimode fibres capable of carrying more than one signal). By the use of the holey fibre performs, the present application allows the use of dispersed species
5 that would normally interfere with the sensitive and generally incompatible processes.

Thus the present invention allows the use of active species, such as exemplified by rare earth amplifiers in the production of graded/stepped multimode fibres while at the same time avoiding the problems faced by attempting to simultaneously a graded index profile in a fibre at the same time as introducing functional species into the polymer.

10 For example, if one wished to prepare a graded index profile fibre containing rare earth amplifiers by the method of the prior art, one would need to introduce the rare earth species before polymerisation, then attempt to use the differential polymerisation techniques required to introduce the refractive index gradient across the fibre. Such processes are sensitive enough at the best of times and the presence of metallic species
15 would be expected to interfere greatly with these (which are often metal catalysed).

Thus, the method of the present invention in using holey POFs, allows the separation of the step of introducing functionality and the step of determining refractive index. Because, in the present invention the functionality determining step is distinct from refractive index determining step, it is possible to use conventional methods or
20 conventional chemistry to functionalise, the POF material, then by the use of a holey perform prepared from that material to introduce a graded refractive index into a perform (by any conventional physical or chemical means) which is then drawn into a holey fibre with a profile corresponding to the polymer. Thus, the present invention deconvolutes the processes of functionalising fibre and forming the refractive index profile.

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In another preferred alternative, the functional species is molecular. More preferably, the molecular species is one or more of a mechanical property modifier or an optical property modifier. Preferred mechanical property modifiers include plasticisers. Preferred optical property modifiers include fluorescing species, electro-optic, acousto-
5 optic, magneto-optic or piezo-optic species.

Examples of plasticisers include, but are not limited to: benzyl ether, benzyl 2-nitrophenyl ether, bis(1-butylpentyl) adipate, bis(1-butylpentyl) decane- 1,10-diyl diglutarate, bis(2-ethylhexyl) adipate, bis(2-ethylhexyl) sebacate, 1-chloronaphthalene, chloroparaffin, 1-decanol, dibutyl phthalate, dibutyl sebacate, dibutyltin dilaurate, 1,2-
10 dimethyl-3-nitrobenzene, dioctyl phenylphosphate, dipentyl phthalate, 1-dodecanol, dodecyl 2-nitrophenyl ether, [12(4-ethylphenyl)dodecyl]2-nitrophenyl ether, 2-fluorophenyl 2-nitrophenyl ether, 1-hexadecanol, 10-hydroxydecyl butyrate, 2-nitrodiphenyl ether, 2-nitrophenyl octyl ether, 2-nitrophenyl pentyl ether, 1-octadecanol, octyl [2-(trifluoromethyl)phenyl] ether, 5-phenyl-1-pentanol, 1-tetradecanol, tetraundecyl
15 benzhydrol-3,3',4,4'-tetracarboxylate, tetraundecyl benzophenone-3,3',4,4'-tetracarboxylate, tributyl phosphate, trioctylphosphine oxide, tris(2-ethylhexyl) phosphate, tris(2-ethylhexyl) trimellitate.

Electro-optic materials include compounds such as 4-(N,N-diethylamino)-2-fluoro-(Z)-methyl-(E)-nitrostyrene.

20 In yet another preferred alternative, the dispersed species is particulate.

The dispersion of the functional species may also be enhanced by the addition of other dispersed functional species in the preform or fibre, such as surfactants.

The dispersion of the functional species may be assisted or controlled by the preselection of polymers having groups capable of interacting with said functional species.

25 Preferred groups include chelating groups and/or acid groups.

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Alternatively, the dispersed species may be a particulate or colloidal species, preferably selectable from metal oxides, semiconductor particles and quantum dots.

According to a sixth aspect the invention provides a reactable polymeric optical fibre having a predetermined cross-section with at least a first discrete region and a second
5 discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material including at least one reactable functionality.

Preferably the second discrete optical element is a void.

Preferably, the reactable polymeric optical fibre is adapted to modify on reaction a predetermined property of the polymer optical fibre.

10 In one particularly preferred embodiment, the reactable polymeric optical fibre includes one or more of a double bond and an epoxy group. In this case, preferably modification takes place in discrete locations by way of the application of UV light to discrete locations to double bonds reactable by cross-linking under the influence of UV light. Preferably, the UV light is applied in discrete locations by the use of phase masks to
15 form a Bragg grating.

According to a seventh aspect the invention provides a method of forming a polymer optical fibre of the present invention including the steps of:
dispersing a functional species in a polymer precursor;
forming a polymer from said polymer precursor;
20 shaping an optical fibre preform from said polymer; and
drawing said polymer optical fibre from said preform.

According to an eighth aspect, the invention provides a method of forming a polymer optical fibre of the present invention including the steps of:
dispersing a functional species in a polymer precursor;
25 shaping an optical fibre preform from said polymer precursor;

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forming a polymer from said polymer precursor; and
drawing said polymer optical fibre from said preform.

Preferably, the polymer precursor has a polymerisable portion and a functional group portion.

5 Preferably the polymer precursor is a reactable species and polymer optical fibre is reactable.

Preferably the polymer precursor has a preselected property adapted for optical use.

In one embodiment, the polymer with a preselected property is a polymer with a special refractive index, a polymer with a special optical non-linearity property or a
10 polymer with groups with special opto-mechanical, electro-mechanical, acousto-optical or magneto-optical properties.

In an alternative embodiment the polymer with a preselected property is one or more of a free radical polymer, a condensation polymer, a catalytically formed polymer, ROMP polymers, an enzymatically formed polymer, a biopolymer, a sol-gel polymer and a
15 chain addition polymer.

In a further alternative embodiment, the polymer with a preselected property is one or more of a liquid crystal polymer, a polymer with high mechanical strength, a highly flexible polymer, a UV resistant polymer or a solvent resistant polymer.

Atomic species can either be dispersed between polymer chains, or the polymers may
20 have groups, such as acid groups or chelating groups that specifically help disperse atomic species such as metal ions.

Some polymers allow easy dispersion of molecular species between the polymer chains. This feature depends upon the thermodynamics of mixing of the molecular species and the polymer. Other polymers have specific chemical groups that interact with
25 molecules, e.g. chelating groups, which help disperse molecular species. Species that may

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be usefully added to polymer fibers included plasticizing agents to help fibre mechanical properties, surfactants to help disperse particulate material, and molecules with particular optical functions such as fluorescing species or electro-optic, acousto-optic, magneto-optic or piezo-optic molecules.

5 Some polymers are particularly good at aiding the dispersion of particulate or colloidal species, via either physical or chemical interaction with the particles to be dispersed. Useful particulate dispersions include metal oxides, semiconductor particles and even quantum dots.

 The invention also provides a drawable polymer preform having a predetermined
10 cross-section including at least one polymeric material having at least one functional species bound thereto.

 The invention provides a polymeric optical fibre having a predetermined cross-section including at least one polymeric material having at least one functional species bound thereto.

15 The invention provides a method of forming a polymer optical fibre having a predetermined cross-section from a polymer preform including the steps of:

 preparing a functionalised polymer precursor composition, said composition including a polymer precursor component having a polymerisable portion and a functional group portion;

20 forming a polymer from said polymer precursor composition;
 shaping an optical fibre preform from said polymer; and
 drawing said polymer optical fibre from said preform.

 The invention provides a method of forming a polymer optical fibre having a predetermined cross-section from a polymer preform including the steps of:

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preparing a functionalised polymer precursor composition, said composition including a polymer precursor component having a polymerisable portion and a functional group portion;

shaping an optical fibre preform from said polymer precursor;

5 forming a polymer from said polymer precursor; and

drawing said polymer optical fibre from said preform.

In one preferred embodiment, the functionality is on a main chain of the polymer. In an alternative preferred embodiment, the functional group is on a side chain of the polymer.

10 The functionality can be an organic species or inorganic species. In certain highly preferred embodiments, the functionality is an electro optic chromophore or a metal ion.

Polymers may have ionically or covalently bonded species. Many polymers have specific functionality, either on the main chain or side groups. This functionality can be

organic or inorganic species effectively grafted onto the polymer. Useful examples are
15 electro-optic chromophores and metal ions.

The invention provides a reactable polymeric optical fibre having a predetermined cross-section including at least one reactable functionality.

The invention provides a drawable polymer preform having a predetermined cross-section including at least one reactable functionality.

20 In highly preferred embodiments, the polymeric optical fibre includes at least one reactable functionality on a polymeric component. In an alternative embodiment, the polymer optical fibre includes a reactable functionality on a monomeric component.

The invention provides a method of forming a reactable polymer optical fibre having a predetermined cross-section from a polymer preform including the steps of:

25 forming a reactable polymer including a reactable functionality;

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shaping an optical fibre preform from said reactable polymer; and
drawing said reactable polymer optical fibre from said preform.

The invention provides a the invention provides a reactable polymeric optical fibre having a predetermined cross-section including at least one reactable functionality.

5 Preferably, the reactable functionality is adapted to modify on reaction a predetermined property of the polymer optical fibre. Predetermined properties include mechanical and or optical properties of the fibre.

Preferred reactable functionalities include double bonds and epoxy groups, reactable by the use of UV light.

10 In highly preferred embodiments, the modification of the predetermined property takes place in one or more discrete locations in the fibre

In one highly preferred embodiment, the reactable group is a double bond, reactable by cross-linking under the influence of UV light. The UV light is applied in discrete locations by the use of phase masks to form a Bragg grating.

15 The invention provides a method of forming a reactable polymer optical fibre having a predetermined cross-section from a precursor polymer optical fibre including the step of contacting said precursor polymer optical fibre with a reactable species selected to migrate into said precursor polymer optical fibre.

Polymers can accordingly be prepared that have specific functionality after fibre
20 formation. Since pre-formed polymers can be used to form fibers, it is now possible to form fibers with post-production functionality. An example is the use of polymers with residual double bonds, or epoxy groups that can be selectively reacted to change the mechanical or optical properties of the fibre at selected places. A key example is the use of UV light and phase masks to form fiber-Bragg grating in holey polymer fibre by the cross-
25 linking of double bonds. These double bonds could be formed from residual double bonds

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in the polymer from which the fibre is formed, or residual monomer in the fibre, which could be in the fibre during drawing, or added afterwards by soaking, which is helped by the fact that the holey structure has a high effective surface area.

The invention provides a drawable holey polymer preform having a predetermined
5 cross section and formed from a polymer having a preselected physical property adapted for optical use.

The invention provides a polymeric optical fibre having a predetermined cross section including a polymer having a preselected physical property adapted for optical use.

The invention provides a method of forming an polymer optical fibre having a
10 predetermined cross section from a polymer preform including the steps of:

forming a polymer having a preselected physical property adapted for optical use
shaping an optical fibre preform from said polymer; and
drawing said polymer optical fibre from said preform.

Examples of polymers with preselected physical properties are polymers with special
15 refractive indices, polymers with special optical non-linearity properties, and polymers with groups with novel opto-mechanical, electro-mechanical, acousto-optical and magneto-optical properties.

The preselected physical property may also be the mechanism of formation.

Preferred polymers include among others free radical polymers, condensation polymers,
20 catalytically formed polymers, ROMP polymers, enzymatically formed polymers, biopolymers, sol-gel polymers and chain addition polymers. Polymers may also have special physical properties such as liquid crystal polymers, or have mechanical properties such as strength or flexibility, or chemical properties such as UV or solvent resistance.

Previously most high performance POF's for telecommunications purposes have
25 been made by free radical means. This has been because it has been possible to

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manufacture optically transparent polymers in a mould that formed the pre-form, and simultaneously creating refractive index profiles. However, the need to create a refractive index profile has often meant that free radical polymers have been restricted to a small subset of this class of polymers. By way of example high Tg polymers have been required in some instances to ensure that a low molecular weight dopant in the mix, used to form the refractive index profile, does not diffuse through the polymer at operating temperatures (and thus losing the refractive index profile). Also, the formation of the polymers in the pre-form mould has restricted the use of specialty free radical polymers with, for example, novel side group chemistry. In the method of the present invention for forming POF's, free radically formed polymers can be used with more complete control over molecular weight, specific copolymers, side group function, and mixtures with other molecules.

The present invention allows the use of co-polymers that would be difficult to produce uniformly in conventional batch synthesis POF systems (because of composition drift). By being able to produce the polymer in advance it is possible to use semi-continuous (fed) polymerizations that will ensure uniform copolymer composition and good fibre homogeneity.

Condensation polymers have previously not been used extensively to form POF's. This is because this class of polymers is generally highly cross-linked, and thus cannot be drawn from a pre-form into a mould. However, one means of forming holey POF's is the use of direct extrusion of pre-forms or fibers through dies, and the extruded mix can be monomers or oligomeric species, that are precursors to condensation polymers. Formation of the polymer can be achieved post-die via typical means known to those practised in the art, e.g. UV light or heat. Some condensation polymers have extremely useful optical properties such as low absorption of light and good mechanical properties. In addition,

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condensation polymers can often be formed with very useful residual functionality, eg side groups containing double bonds.

Sol-gel polymers are a very special class of condensation polymers that contain Silicon and oxygen in the main chain. These materials have very good optical properties, particularly low absorption of light in the near infrared, but they have not been hitherto readily used in preparing optical fibers.

In addition to the specific types of polymer referred to above, other conventional polymers can be used based on their known physical properties. For most polymers, it was not feasible to produce a light guiding fibre because the processing parameters were not appropriate. Now, however, the present method allows for the use of just about any polymer, and the following properties can be controlled:

Glass transition temperature: A single polymer material means that polymers with low glass transition temperatures can be used. Previously, when a refractive index profile was required, and created with a dopant, a high glass transition (T_g) temperature was required to ensure that the dopant does not diffuse, and thus the refractive index profile lost. Since there is no material profile required in the holey POF of the present invention, low T_g polymers can be used. This allows a broader spectrum of low cost and low absorption polymers to be used. In some cases it is envisaged that drawing of low T_g polymers from pre-forms might require cooling rather than heating.

Melt temperature: High temperature polymers can be used without altering the materials refractive index profile, hence enabling the production of optical fibers for high temperature applications.

Refractive index: Polymers with specific RI Can be formed. One highly useful instance is where the RI of a polymer fibre is matched with that of a silica glass fibre hence

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a fibre component made from POF will have minimum insertion loss when used in conjunction with a silica glass transmission network.

Durability: more choice of durable polymers – mechanical, photochemical, chemical and physical degradation. Further additives can be added as these are no longer susceptible
5 to the polymerization process (eg antioxidants).

Polymers having lower absorptions over the transmission ranges of interest; specific mechanical or processing properties (through the availability of additives)

The present invention may also reduce cost by obviating the need to use very expensive specialty monomer/polymers such as CYTOP. Graded Index Multi-Mode
10 CYTOP material has very high polymer cost.

Other special properties, such as low water absorption, can be obtained simply by the use of known polymers with low water absorption properties.

The present invention also opens the way to the use of polymers with non-linear properties and conducting and semi-conducting polymers.

15 The use of holey fibre technology allows polymers to be drawn at relatively low temperatures (e.g. room temperature to 300°C). At these temperatures it is much easier to draw fibers, and to control the process, and hence the accuracy and precision of the hole structures can be maintained along the length of the fibre.

Polymers can easily be made into a variety of hole sizes and shapes. This can be
20 done by casting, drilling, extrusion and a host of other means, as described previously. This allows a wide variety of fibre design properties to be manufactured that cannot be made in glass holey fibers or POF's prepared by any other methods.

In particular, in another aspect the present invention provides a polymeric optical fibre having an air core a polymeric cladding, and wherein said fibre functions as a band-
25 gap fibre.

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Holey fibres allow the use of a single polymeric material which means that polymers can be used that are 'pre-polymerized'. Generally the polymers used in POF's are polymerized in a mould that shapes the pre-form. This restricts the polymers used to those polymers that can be polymerized in a mould, and that do not have in them highly absorbing catalysts and additives. The ability to use pre-polymerized polymers allows the use of a large range of polymers not previously accessible to POF's, simply because processing of pre-polymerized polymers allows the removal of offending absorbing species prior to the use of these polymers. The advantage of this is that in the search of low loss polymers and low-cost polymers, a much wider variety of polymers are available. The use of pre-polymerized polymers also allows pre-forms and/or fibers to be produced via traditional low-cost polymer processing technologies, such as extrusion and injection molding. This in turn allows the production of holes of any shape, size or distribution.

The scope and breadth of polymers used can now be much greater, resulting from the fact the pre-polymerized polymers can be produced as per usual in the polymer industry, and then the polymers can be processed like normal polymers in the polymer industry, thereby creating holey POF's. Previously many special-function polymers were not able to be used because the process of, say, free radical polymerization of a monomer, would have destroyed, or been incompatible with the special functionality.

The approach of the present invention allows the use of specialty polymers for imparting speciality optical function. In previous methods of forming POF's these polymers could not be used because the polymers could not be manufactured via known means without causing unacceptable optical properties (e.g. optical loss due to absorbing species), or these polymers would be partially or fully de-functionalized or destroyed by the manufacturing process itself. Examples are polymers with special refractive indices,

polymers with special optical non-linearity properties, and polymers with groups with novel opto-mechanical, electro-mechanical, acousto-optical and magneto-optical properties

Holey fibre technology also allows the use of additives to adjust physical properties that would otherwise have been incompatible with the POF production process.

5 The fact that single polymers or polymer mixes can be used, or that pre-polymerized polymers can be used to make holey polymer fibers means that polymer previously not used to make POF's can be utilized.

In addition, the use of a single material for holey polymer fibers allows production of fibers by, for example, the extrusion of monomers, oligomers or other polymer pre-cursors
10 through a precision dies, followed by in-process polymerizations, via means such as UV illumination, heat, and other polymerization techniques. By forming the polymers in this manner, it is possible to make holey POF that are made from polymers that are non-linear, i.e. cross-linked or branched. Previously, in order to draw polymers from pre-forms it has been necessary to use pre-forms made from linear polymers with relatively low molecular
15 weight, so most polymers were thus excluded. This holey fibre technique allows the use of many other amorphous optically transparent polymers.

As discussed in our copending PCT/AU02/00638, one advantage of the preform approach to making holey fibres is that it allows the use of materials that cannot currently be used to make holey fibres. This new technique allows the use of polymers that are
20 polymerised either by bulk polymerisation or by the use of light (eg UV-laser) or other sources. The present invention will also allow the use of polymers made by non-free radical polymerisations, eg condensation polymerisation.

A range of polymers may be used to make the holey fibres or preforms. These are generally those suitable for free radical polymerisation. Specifically
25 polymethylmethacrylate and other methacrylates are common, as are fluorinated

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analogues. In attempts to achieve lower absorption losses much effort has focused on the use of polymer systems which have no C-H bonds. Specifically amorphous Teflons™ (DuPont) and CYTOP™ (Asahi Glass) have been used with some success. All of the above mentioned polymer systems are suitable for the new technique described in this document.

- 5 The new technique can use monomers, oligomers or polymers, or any combination thereof. Polymerisation, if required, can be achieved via chemical, light enhanced or other means. Rapid polymerisation can be achieved by the use of light sensitive polymerisation aids. Additionally polymerisation aids that control molecular weight, such as chain transfer agents, and cross-linking agents can be used; these have benefits in controlling solution
- 10 and polymer viscosity, which may be important in the extrusion process and in the drawing of fibre from the preform.

- While the thermomechanical forming of monomeric/polymeric/oligomeric materials is well known, there is still an element of empirical analysis which must be done to provide the desired result. Indeed, there are a wide variety of parameters for extrusion and
- 15 injection moulding of plastic material as discussed below.

PMMA - EXTRUSION

- ATOFINA Chemicals Inc has various PMMA resins suitable for extrusion under the trade mark Atoglas and Plexiglass™. It is recommended that for extrusion of Plexiglass acrylic resins, barrel and die temperatures should be in the region of around 175°C (350°F)
- 20 to around 250°C (500°F). The dispersed species to functionalise the resin, if a discrete species, can be added to the resin at this stage. Of course, as is clear to persons skilled in the art, these figures will fluctuate depending upon the material which is being extruded, the type and shape of die and the through put.

- Those skilled in the art will be aware that when selecting complexing species for
- 25 metals and the like, it is important to select a complex with regard to the T_g of the

- 25 -

polymeric material. Those skilled in the art will appreciate that the polymeric material is usually drawn at a temperature above its known Tg and accordingly it is desirable to choose a metal-ligand complex which is stable at or above that drawing temperature.

PMMA - INJECTION MOULDING

5 For injection moulding of PMMA, mould temperatures around 40 to 80°C are suggested depending upon the type of mould, with the material temperature should be around 200 to 250°C. The dispersed species to functionalise the resin, if a discrete species, can be added to the resin while it is molten and mixed by stirring or the like. As temperature increases, molecular orientation and internal stresses decrease, however, the risk of sink spots increase. Generally high injection pressures are required due to the poor flow properties of PMMA and it may be necessary to slowly inject the material to maintain the correct flow.

TEFLON - INJECTION MOULDING AND EXTRUSION

Once again, however, if material other than PMMA is used, different parameters may be required. For example, using Teflon® AF amorphous fluoropolymer resin as supplied by E. I. du Pont de Nemours and Company is suitable for both extrusion and injection moulding.

Teflon® AF can also be formed at relatively low temperatures by extrusion or injection moulding in typical fluoropolymer moulding equipment. Teflon® AF 1600 for example, has typical extrusion/moulding temperatures of around 240 to 270°C (464 to 527°F) Teflon® AF 2400 has extrusion/moulding temperature of around 340°C to 360°C (644°F to 680°F) processing above 360°C is to be avoided since the polymer begins to decompose at this level.

if a discrete species is used to functionalise the resin, it can be added to the resin when it is molten, although those skilled in the art will be careful to ensure that a suitable

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dispersed species is chosen so as not to thermally degrade at a temperature below the processing temperature of the resin.

As with PMMA, it is highly desirable to have corrosion resistant tooling for the die and associated equipment. Both Teflon® AF 1600 and 2400 have been shown suitable for
5 fibre optics.

It will be appreciated by persons skilled in the art that the present invention provides a significant commercial advance over the prior art. Variations and other embodiments of the inventive process and products resulting therefrom may be made without departing from the spirit or scope of the inventive idea.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. The use of an at least partially polymerised preform having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical
5 refractive indexes for drawing into a fibre having a corresponding cross-section, and wherein said first discrete region is formed from an optically suitable material which includes at least one functional species dispersed therethrough.
2. The use according to claim 1 wherein said second discrete optical element is a void.
3. A drawable polymer preform having a predetermined cross-section with at least a
10 first discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material which includes at least one functional species dispersed therethrough.
4. A drawable polymer preform according to claim 3 wherein said predetermined cross-section is a precursor profile for a holey polymer fibre.
- 15 5. A drawable polymer preform according to claim 3 or 4 wherein said second discrete region is a void.
6. A drawable polymer preform according to any one of claims 3 to 5 wherein said polymer is selected from the group consisting of polymethyl methacrylate, polymethylmethacrylate/polystyrene, siloxane, fluoropolymers, fluoroacrylates,
20 fluoroacrylate esters, fluorinated polyimides, polytetrafluoroethylene, fluorosilicones CYTOP™ and THV™.
7. A drawable polymer preform having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material which
25 includes at least one functional species bound thereto.

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8. A drawable polymer preform having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material which includes at least one reactable functionality.
- 5 9. A drawable polymer preform according to claim 8 wherein reactable functionality is on a polymeric component.
10. A drawable polymer preform according to claim 9 wherein reactable functionality is on a monomeric component.
11. A polymeric optical fibre having a predetermined cross-section with at least a first
10 discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material which includes at least one functional species dispersed therethrough.
12. A polymeric optical fibre according to claim 11 wherein said second discrete optical element is a void.
- 15 13. A polymeric optical fibre according to claim 11 or 12 having a graded refractive index profile.
14. A polymeric optical fibre according to any one of claims 11 to 13 in the form of a multimode fibre.
15. A polymeric optical fibre according to any one of claims 11 to 14 wherein said
20 polymer is selected from the consisting of polymethyl methacrylate, polymethylmethacrylate/polystyrene, siloxane, fluoropolymers, fluoroacrylates, fluoroacrylate esters, fluorinated polyimides, polytetrafluoroethylene, fluorosilicones CYTOPTM and THVTM.
- 25 16. A polymeric optical fibre according to any one of claims 11 to 15 wherein functional species is an optical property modifier.

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17. A polymeric optical fibre according to claim 16 wherein said optical property modifier is selected from fluorescing species, electro-optic, acousto-optic, magneto-optic or piezo-optic species.
18. A polymeric optical fibre according to claim 11 including a dispersed species,
5 wherein said dispersed species is a mechanical property modifier.
19. A polymeric optical fibre according to claim 18 wherein said mechanical property modifier is a plasticisers or surfactant.
20. A polymeric optical fibre according to claim 11 formed from a polymer having groups capable of interacting with said functional species.
- 10 21. A polymeric optical fibre according to claim 20 including groups capable of interacting with said functional species include pendant chelating groups and/or acid groups.
22. A polymeric optical fibre according to any one of claims 11 to 21 wherein said functional species is an optical amplifier.
- 15 23. A polymeric optical fibre according claim 22 wherein said functional species is one or more rare earth elements in complexed or uncomplexed form.
24. A polymeric optical fibre according to claim 23 wherein the rare earth metal is in complexed form, with one or more organic ligands.
25. A polymeric optical fibre according to claim 24 wherein the ligands are selected
20 from phenanthroline, bipyridine, or beta diketone ligands.
26. A polymeric optical fibre according to claim 25 wherein the ligand is 6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octanedion (FOD).
27. A polymeric optical fibre according to claim 26 wherein the functional species is EuFOD or ErFOD.

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28. A polymeric optical fibre according to claim 23 wherein the rare earth element is one or more of erbium, praseodymium or tantalium.
29. A polymeric optical fibre according to claim 11 wherein said dispersed species is a particulate or colloidal species.
- 5 30. A polymeric optical fibre according to claim 29 wherein the particulate dispersion is selectable from metal oxides, semiconductor particles and quantum dots.
31. A reactable polymeric optical fibre having a predetermined cross-section with at least a first discrete region and a second discrete region with non identical refractive indexes, and wherein said first discrete region is formed from an optically suitable material
- 10 including at least one reactable functionality.
32. A reactable polymeric optical fibre according to claim 31 wherein said second discrete optical element is a void.
33. A reactable polymeric optical fibre according to claim 31 or 32 adapted to modify on reaction a predetermined property of the polymer optical fibre.
- 15 34. A reactable polymeric optical fibre according to any one of claims 31 to 33 including one or more of a double bond and an epoxy group.
35. A reactable polymeric fibre according to claim 33 or 34 wherein modification takes place in discrete locations by way of the application of UV light to discrete applications to double bonds reactable by cross-linking under the influence of UV light.
- 20 36. A reactable polymeric fibre according to claim 35 wherein the UV light is applied in discrete locations by the use of phase masks to form a Bragg grating.
37. A method of forming a polymer optical fibre as defined in any one of claims 11 to 30 including the steps of:
- dispersing a functional species in a polymer precursor;
- 25 forming a polymer from said polymer precursor;

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shaping an optical fibre preform from said polymer; and

drawing said polymer optical fibre from said preform.

38. A method of forming a polymer optical fibre as defined in any one of claims 11 to 30 including the steps of:

5 dispersing a functional species in a polymer precursor;

shaping an optical fibre preform from said polymer precursor;

forming a polymer from said polymer precursor; and

drawing said polymer optical fibre from said preform.

39. A method according to claim 37 or 38 wherein the polymer precursor has
10 a polymerisable portion and a functional group portion;

40. A method according to claim 38 or 38 wherein the polymer precursor is a reactable species and polymer optical fibre is reactable.

41. A method of forming a holey polymer fibre from a polymer with a preselected property adapted for optical use including the steps of forming a holey preform from said
15 polymer and thermomechanically forming a holey polymer fibre from said preform.

42. A method according to claim 41 wherein the polymer with a preselected property is a polymer with a special refractive index, a polymer with a special optical non-linearity property or a polymer with groups with special opto-mechanical, electro-mechanical, acousto-optical or magneto-optical properties.

20 43. A method according to claim 41 wherein the polymer a preselected property is one or more of a free radical polymer, a condensation polymer, a catalytically formed polymer, a ROMP polymers, an enzymatically formed polymer, a biopolymer, a sol-gel polymer and a chain addition polymer.

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44. A method according to claim 41 wherein the polymer a preselected property is one or more of a liquid crystal polymer, a polymer of high mechanical strength, a highly flexible polymer, a UV resistant polymer or a solvent resistant polymer.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU02/01006

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : G02B 6/16, 6/20, C03B 37/012, 37/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI, JAPIO: IPC G02B 6/-, C03B 37/- & keywords [(preform?, fiber?, fiber?)(s)(plastic, polymer+); (hole?, channel?, void+, air, hollow, index, indices; (1) functional+, nonlinear+, rare earth, amplif+, fluoresc+, (electro, acousto)(w)(optic+), particulate, colloidal, sol-gel?; (2) react+, double bond?, epox+, cross link+, free radical?; grating?, photosensitiv+]; (3) [(holey, photonic crystal, microstructur+) (2w)(fiber?, fiber?, preform?); polymer+, plastic] INSPEC: keywords		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5450232 A (SASAKI <i>et al.</i>) 12 September 1995 Col. 1 line 65 - col. 2 line 52, col. 4 line 58 - col. 5 line 46, figure 1	1, 3, 6, 7, 11, 13-17, 22, 37-39
X	TAGAYA A. <i>et al.</i> , "POLYMER OPTICAL FIBER AMPLIFIER", APPLIED PHYSICS LETTERS, vol. 63, No. 7, 16 August 1993, pages 883-884 The whole document	1, 3, 6, 7, 11, 13-17, 22
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 1 November 2002		Date of mailing of the international search report 08 NOV 2002
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer IRINA TALANINA Telephone No : (02) 6283 2203

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/01006

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 473496 B (FRANCE TELECOM) 5 July 1995 Abstract, claims, figure 1	1, 3, 6, 7, 11, 15-17
X	GARVEY D.W. <i>et al.</i> , "SINGLE-MODE NONLINEAR-OPTICAL POLYMER FIBERS", JOURNAL OF OPTICAL SOCIETY OF AMERICA B, vol. 13, No. 9, September 1996, pages 2017-2023 Sec. 2 "Fiber Fabrication" & figure 9, Sec. 6 "Conclusion"	1, 3, 6, 7, 11, 15-17, 20-22
X	KURIKI K. <i>et al.</i> , "HIGH-EFFICIENCY ORGANIC DYE-DOPED POLYMER OPTICAL FIBER LASERS", APPLIED PHYSICS LETTERS, vol. 77, No. 3, 17 July 2000, pages 331-333 The whole document	1, 3, 6, 7, 11, 13-17, 22, 37-39
P, X	JP 2002-171019 A (JAPAN SCIENCE & TECHNOLOGY CORP) 14 June 2002 Abstract, translation & figure from www1.ipdl.jpo.go.jp/PA1/cgi-bin/PA1INDEX	1, 3, 6, 7, 11, 13-17, 20-27, 37-39
P, A	US 6301421 B (WICKHAM <i>et al.</i>) 9 October 2001 The whole document	1-7, 11-30, 37-40
X	XIONG Z. <i>et al.</i> , "HIGHLY TUNABLE BRAGG GRATINGS IN SINGLE-MODE POLYMER OPTICAL FIBERS", IEEE PHOTONICS TECHNOLOGY LETTERS, vol. 11, No. 3, March 1999, pages 352-354 The first & the last paragraphs in Sec. II "Fabrication of POF Gratings"	8-10, 31, 33- 36
X	PENG G. <i>et al.</i> , "POLYMER OPTICAL FIBER PHOTSENSITIVITY AND HIGHLY TUNABLE OPTICAL FIBER BRAGG GRATINGS", SPIE - Int. Soc. Opt. Eng. Proceedings of SPIE - The International Society for Optical Engineering, USA, vol. 4110, 2000 pages 123-138 (INSPEC Accession Number 006920266) Abstract	8-10, 31, 33- 36
P, X	LIU H.Y. <i>et al.</i> , "THERMAL STABILITY OF GRATINGS IN PMMA AND CYTOP POLYMER FIBERS", OPTICS COMMUNICATIONS, vol. 204, 1 April 2002, pages 151-156 Sec. 2 "Fabrication of gratings in CYTOP fiber slab"	8-10, 31, 33- 36
P, A	WO 01/63345 A (UNIVERSITY OF PITTSBURGH OF THE COMMONWEALTH SYSTEM OF HIGHER EDUCATION) 30 August 2001 The whole document	31, 34

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU02/01006

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	VAN EIJELENBORG M.A. <i>et al.</i> , "MICROSTRUCTURED POLYMER OPTICAL FIBRE", OPTICS EXPRESS, vol. 9, No. 7, 24 September 2001, pages 319-327 3 rd paragraph in Sec. 4 "Advantages of microstructured polymer optical fibre"	41-44
P, X	WO 02/16984 A (THE UNIVERSITY OF SYDNEY) 28 February 2002 Page 3 lines 11-21, page 8 lines 19-30, figure 4	41, 42
P, X	ARGYROS A. <i>et al.</i> , "RING STRUCTURES IN MICROSTRUCTURED POLYMER OPTICAL FIBRES", OPTICS EXPRESS, vol. 9, No. 13, 17 December 2001, pages 813-820 Sec. 3 "Microstructures and ring structures"	41, 42
A	US 3516239 A (KENJI FUKUDA <i>et al.</i>) 23 June 1970 Col. 1 lines 15-52, col. 4 line 72 - col. 5 line 34, claim 1, figure 1	41, 44
P, A	GB 2365992 A (UNIVERSITY OF SOUTHAMPTON) 27 February 2002 Abstract, page 3 line 1 - page 4 line 17, figures 4, 10	41-44

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU02/01006

Box I Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos :
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos :
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos :
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU02/01006**Supplemental Box**

(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No II:

The international application does not comply with the requirements of unity of invention because it does not relate to one invention only (or to a group of inventions so linked as to form a single general inventive concept). In assessing whether there is more than one invention claimed, a consideration has been given to those features which can be considered to be "special technical features". These are features which potentially distinguish the claimed combination of features from the prior art. Where different claims have different special technical features, they define different inventions. The International Searching Authority has found that there are three different inventions as follows:

- (1) Claims 1-7, 11-30, 37-40 are directed to a polymer preform and a polymeric optical fibre. It is considered that a first discrete region formed from a material which includes at least one functional species comprises a first "special technical feature".
- (2) Claims 8-10, 31-36 are directed to a polymer preform and a polymeric optical fibre. It is considered that a first discrete region formed from a material which is reactable comprises a second "special technical feature".
- (3) Claims 41-44 are directed to a method of forming a holey polymer fibre. It is considered that a thermomechanical formation of the holey polymer fibre from a preform comprises a third "special technical feature".

These groups of claims do not share either of the technical features identified. The common concept linking together these groups of claims is a polymer preform for a polymeric optical fibre. However, this common feature is generic in the art. Consequently, the common feature does not constitute "a special technical feature" since it makes no contribution over the prior art. Since there exists no other common feature which can be considered as a special technical feature, a "technical relationship" between the inventions, as defined in PCT Rule 13.2, does not exist. Accordingly, the international application does not relate to one invention only.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU02/01006

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member	
US 5450232	EP 586713	JP 5275789	WO 9319505
EP 473496	FR 2666046	US 5182783	
JP 2002171019	NONE		
US 6301421	NONE		
WO 200163345	AU 200138634	US 2002008229	
WO 200216984	AU 20009688	AU 200172230	
US 3516239	DE 1669544	GB 1169106	NL 6703905
GB 2365992	AU 200178595	WO 200214946	
END OF ANNEX			